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RECENT DEVELOPMENTS IN HALF-METALLIC MAGNETISM

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The compound PtMnSb is a half-metallic ferromagnet and its unusual band structure is intimately connected with the high Magneto Optical Kerr Effect (MOKE). In this paper it will be discussed how various types of substitutions can modify this band structure and lead to possible enhancement of the MOKE transitions. Novel half-metallic systems will be presented comprising half-metallic ferrimagnets and half-metallic antiferromagnets.

1. Introduction

The Magneto-optical Kerr Effect (hereafter referred to as MOKE) has been studied extensively over the past several years. The highest Kerr rotation of all metallic systems at room temperature is realized in the compound PtMnSb [1]. The basis of this high MOKE is

found in the unusual electronic structure of PtMnSb: it is a member of the class of so-called Half-Metallic Materials [2]. Half-metallic materials are defined as materials showing normal metallic behaviour for one spin direction, while at the same time being insulators (or semiconductors) for the opposite spin direction. The unusual electronic structure is an ingredient for the high

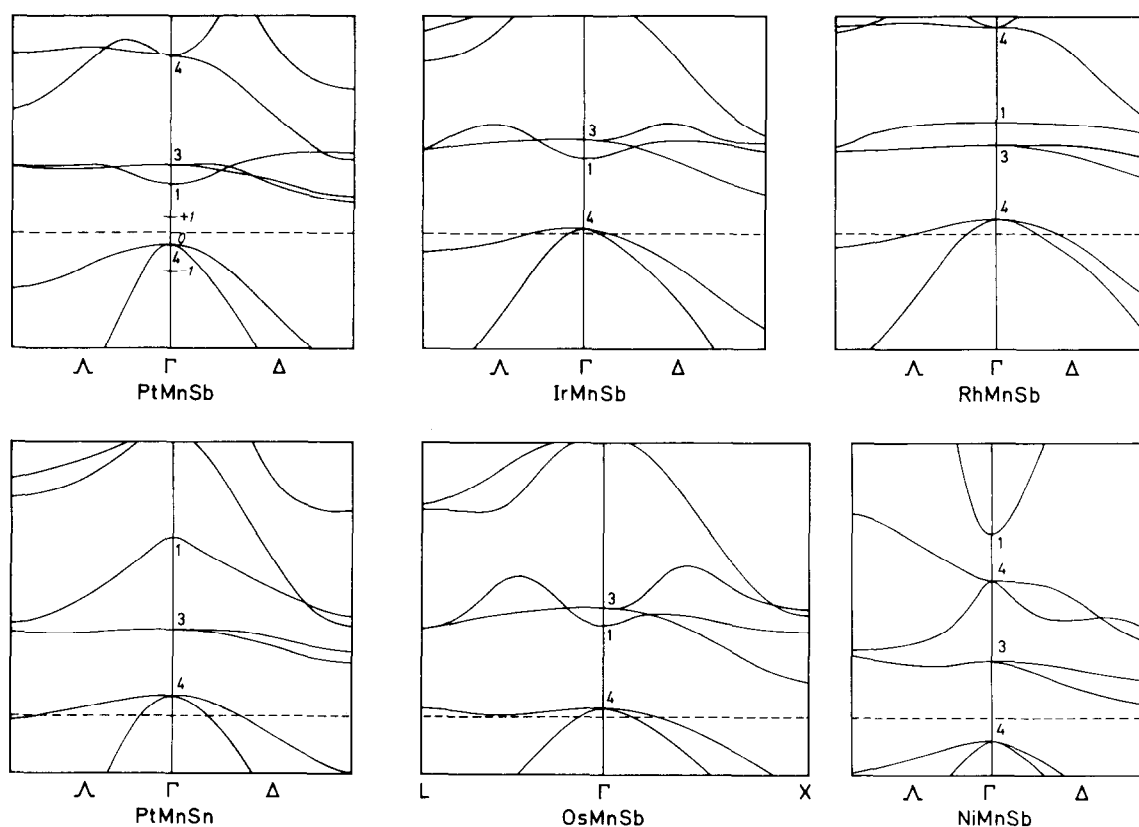


Fig. 1. Electronic structure of the minority spin direction around Γ for PtMnSb, IrMnSb, RhMnSb, PtMnSn, OsMnSb and NiMnSb respectively. The spin-orbit splitting at Γ is indicated in the case of PtMnSb.

MOKE in PtMnSb [3]. Its explanation is as follows: Consider the minority spin electronic structure (fig. 1). The Fermi level (which position is fixed by the majority spin electrons) is positioned just above the top of the valence band. This valence band has dominantly antimony p-character. Spin-orbit interaction of the top of the valence-band at Γ will split this level into three equidistant states with $m = -1$, $m = 0$ and $m = +1$ with increasing energy and the $m = -1$ state will be positioned above E_F . An optical transition is possible to the singlet final state at Γ , with symmetry label 1. In a conventional material, the excitations from the $m = -1$ and $m = +1$ initial states would cancel completely. Here excitations from the $m = +1$ level are eliminated, because this level, being empty now, cannot serve as an initial state for optical transitions any more. Thus, no cancellation of the rotation of the excitation from the $m = -1$ level occurs.

In optimizing the magneto-optical properties one has to realize that in PtMnSb the contribution from the uncompensated excitation around Γ is large, but only a small amount of electrons are involved. The prime goal in optimizing MOKE properties should be to increase the number of electrons involved in the rotationally active excitation. This will be the subject of the next section. We need to be careful, however. The MOKE is determined by the lack of cancellation of left turning and right turning excitations through the non-diagonal matrix element δ of the dielectric tensor ϵ . This is not the only factor determining the MOKE, however. In fact the Kerr rotation and ellipticity ϕ_k and ϵ_k , respectively, are given by:

$$\phi_k + i\epsilon_k = i\delta/\epsilon_r^{1/2}(1 - \epsilon_r).$$

It is tempting to concentrate on optimizing δ (by suitable doping, as we will see), but one has to realize that the introduction of disorder will enhance ϵ_r and thus *reduce* the MOKE at the same time, and there is no guarantee that the net effect will be favourable. For this reason it is also important to focus on new half-metallic systems. We will discuss this line in the second part of this paper. All calculated band structures in this paper employed the self-consistent, all electron ASW method as described by Williams, Kuebler and Gelatt [4].

2. Modification of the band structure of PtMnSb

In order to involve more electrons in the magneto-optically active transition, the Fermi level has to be brought down towards the top of the valence-band or even overlapping the top of the valence band in the case without spin-orbit splitting. This way the number of electrons showing an uncompensated transition can be enhanced, because the number of compensating transitions is depleted. A too strong lowering of the Fermi energy is unfavourable, however, since the moment the Fermi energy crosses the lowest singlet of the

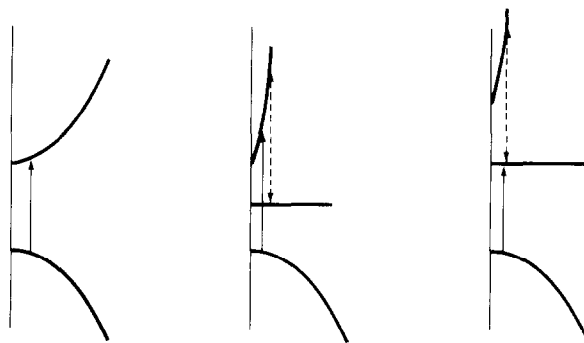


Fig. 2. Interference from a third state with the symmetry of the initial state. Left: Unperturbed situation. Middle: interfering state *inbetween* initial and final state. Its interaction with the final state *reduces* the JDOS for the optical transition *without* gain in oscillator strength. Right: Interfering state *above* final state. Its interaction with the final state *enhances* the JDOS *without* a corresponding loss in oscillator strength. Solid arrows: optical transition. Broken arrows: interaction between interfering and final states.

spin-orbit-split top of the valence band, the number of "active" electrons also is diminished. Thus PtMnSn is unfavourable (fig. 1) and we have to look at intermediate case, for example $\text{NiMnSb}_{1-x}\text{Sn}_x$ or $\text{PtMnSb}_{1-x}\text{Sn}_x$. It is not clear beforehand, whether this substitution will give the required effect. It is possible that locally around a Sn atom a situation will occur which resembles the electronic structure of NiMnSn and around a Sb atom the situation will remain unchanged. With increasing x in $\text{NiMnSb}_{1-x}\text{Sn}_x$ the concentration of both cases will change, but we will not achieve a gradual rigid band-like lowering of the Fermi energy with respect of a relatively unchanged valence band. In order to test the behaviour we calculated the band structure of a hypothetical ordered alloy $\text{Ni}_4\text{Mn}_4\text{Sb}_3\text{Sn}$. This structure allows the highest concentration of Sn without the occurrence of Sn pairs. The result is that at Γ the top of the valence band approaches E_F closely. There are no split-off Sn-like states. We conclude that there is no risk in these systems for finding split-off states from the valence band and in principle one can fine-tune the position of the valence band with respect to E_F by suitable doping.

Final states are as important as initial states in an optical transition, however.

Much can be learned about the strength of an optical transition from the free electron model. Two factors determine the strength of an optical transitions: the oscillator strength and the Joint Density of States (JDOS). Deviations from the free-electron model can be expressed in $k \cdot p$ perturbation theory. Since the same (p) matrix elements describe the deviations of the band structure from the free-electron bands *and* the oscillator strengths this is a useful tool for analyses. Consider two free electron states which originate from the first zone. Since these bands are parallel, the JDOS is large, but

since they are free electron states, there is no oscillator strength and hence no absorption. If one allows for a moderate interaction between the states the JDOS will be diminished, of course, but since there is an oscillator strength there will be absorption. In the limit of strong interaction the JDOS will vanish and we again enter a region of no absorption. The $k \cdot p$ model thus shows that JDOS and oscillator strengths are not independent quantities. But in general there are many more states than just two. Let us consider the influence of a third state with the same symmetry of the initial state, say (fig. 2). Its influence is depending on its energy-position now. If the third level is positioned *in between* initial and final states the interaction with the final state will *decrease* the JDOS of the excitation *without* the corresponding gain in oscillator strength as compared to the two-level situation. This situation is clearly unfavourable. If on the other hand, the perturbing level is located *above* the final states, its interaction with the final state will *enhance* the JDOS of the optical transition *without* sacrificing oscillator strength. The same arguments hold for intervening states with the symmetry of the final state. We can summarize this rule as follows: "In general a strong absorption is expected if there are no states in between initial and final states with the symmetry of either initial or final state". Exceptions to this rule are very well possible, but in general the rule should hold fairly well. This rule explains directly why NiMnSb, even doped with Sn to fine-tune the position of E_f has no high MOKE [5]: The Mn-d levels (empty) of symmetry 4 interfere in the optical transition between the top of the valence band and level 1. In PtMnSb the position of level 1 and the Mn-d levels are reversed, hence the strong absorption in PtMnSb. Fig. 1 shows the band structure of IrMnSb; RhMnSb and OsMnSb for the minority-spin-direction around Γ . IrMnSb shows final states very similar as PtMnSb, so the system $\text{Pt}_{1-x}\text{Ir}_x\text{MnSb}$ should be interesting. Unfortunately the preparation of such compounds in the Cl_b structure has been unsuccessful up till now. RhMnSb is also promising, the empty Mn-d states are lower in energy here (the level marked 4 highest in energy) and, consistent with the rule derived above, makes the level marked 1 (a level of primarily s character!) almost dispersionless with a corresponding increase in JDOS for the excitation from the valence-band to state 1. Experimental work on $\text{Pt}_{1-x}\text{Rh}_x\text{MnSb}$ is underway.

3. Other half-metallic systems

In fig. 3 we show the electronic structure of Fe_3O_4 , a material whose magneto optical properties are also widely studied. It is a half-metallic ferrimagnet with an energy gap of 0.76 eV in the majority spin-direction. These results are in agreement with the earlier work of Yanase and Siratori [6]. The magneto-optical properties of Fe_3O_4 and related compounds are subjects in their

own right. We will concentrate here on the Heusler alloys only. Besides PtMnSb, the band structure of the isoelectronic isostructural compounds NiMnSb shows also half-metallic properties. Interchange of the Ni and Mn in this compound destroys the halfmetallic properties [7]. Substitution of Sn for Sb in PtMnSb leads to a rigid band-like shift of the Fermi level and thus to a destruction of the half-metallic properties. Kuebler, however, found that the band structure of the isostructural isoelectronic compounds CoMnSb is half-metallic [8]. What will happen if we substitute Fe for Co in this compound? From considerations of the magnetic moment it seems unlikely that FeMnSb is half-metallic. We have to realize that the spin-only value of the magnetic moment is necessarily an integral number for a half-metallic system. Since the number of electrons in the semiconducting spin-direction is integral and the total number of electrons is integral the number of electrons for the metallic spin direction is necessarily also integral, hence the difference between the number of electrons for the two spin directions is also integral. For NiMnSb this number is 4, for CoMnSb it is 3. FeMnSb – if it were half-metallic – would have a moment of $2\mu_B$ and it is doubtful whether manganese would tolerate such a strong reduction of its magnetic moment. But according to our calculations FeMnSb is half-metallic: it orders *ferrimagnetically* with a moment of $3.5\mu_B$ on manganese and a moment of $1.5\mu_B$ on iron, oriented anti-parallel. In this way the total moment is $2\mu_B$, indeed, while the local moment on Mn is substantially larger. We wish to emphasize that this behaviour implies a *novel mechanism to the (super) exchange coupling*: The only way for FeMnSb to maintain the energy gained by the formation of the gap in the minority spin direction is to order ferrimagnetically, the ferromagnetic state having larger total energy and being metallic for

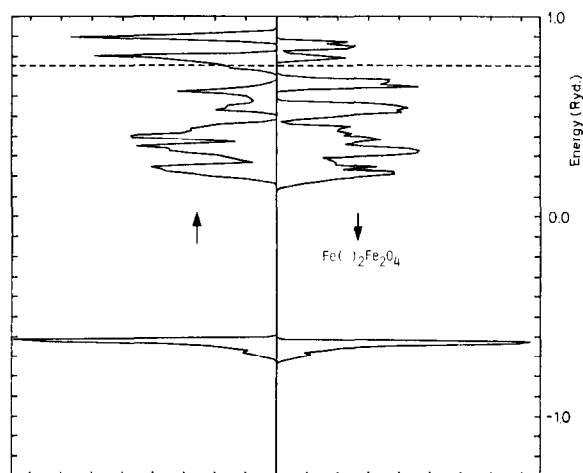


Fig. 3. Density of states of Fe_3O_4 . Energy gap of 0.76 eV in the majority spin direction; magnetic moment $4\mu_B$.

both spin directions. FeMnSb does not crystallize in the Heusler Cl_b structure. Recent experimental results showed, however, that $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ can be prepared in the Heusler Cl_b structure with x approaching close to 1. A study of the physical properties of these compounds is in progress.

Substitution of Mn for Fe in FeMnSb would lead to the compound Mn_2Sb which is also half metallic in its hypothetical Cl_b structure and is a ferrimagnet with a moment of $1\mu_B$. Very interesting is the case of CrMnSb. Its electronic structure calculated in the Cl_b structure is that of a half-metallic antiferromagnet: i.e. a compound showing no net magnetic moment but still with a complete asymmetric electronic structure for both spin directions: one of a metal and one of a semiconductor. If this behaviour persists in the real structure it would give a quite different explanation for the so-called exchange-inversion transition in CrMnSb. Experimentally CrMnSb undergoes an antiferromagnetic to ferromagnetic transition close to room temperature. In AMnSb the total magnetic moment is steadily reduced going from A = Ni to A = Cr, because of an increase in moment on the A site antiparallel to the Mn moment. The coupling is antiparallel in order to maintain the energy gap in the minority-spin direction. But for this there is a price to be paid. The magnetic coupling due to normal superexchange favours a ferromagnetic coupling between the A moment and the Mn moment. This energy increases with increasing moment on the A site and in CrMnSb it just balances the energy-gain of the semiconducting gap. Thus the exchange inversion transition in CrMnSb may very well be a semiconductor to metal transition but for one spin direction only! We are studying the electronic structure of these compounds in their real structure and hope to report on them in the near future.

4. Concluding remarks

We have discussed possible changes of the electronic structure of half-metallic ferromagnets due to the partial replacement of one of the constituting elements. We have shown that fine-tuning of the relative positions of E_f and the top of the valence band does not always lead to an enhancement of the Kerr effect. A reduction of the latter effect will occur in particular when electron-states arise in between the initial and final states of the magneto-optical transitions. Novel type of compounds have been presented comprising half-metallic ferrimagnets and half-metallic antiferromagnets. In these compounds the anti-ferromagnetic coupling is intimately connected with the energy gap in the minority band, representing a new type of (super)exchange coupling.

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